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AT BE CH DE ES FR GB IT LI LU NL(71) Applicant: PELT & HOOYKAAS B.V.
1 Bijlstraat
NL-3087 AA Rotterdam (NL)(72) Inventor: Hooykaas, Carel Willem Jan
44, Oranjelaan
NL-3062 BT Rotterdam (NL)(74) Representative: van der Kloet-Dorleijn,
Geertruida W.F., Drs. et al
van Exter Polak & Charlouis B.V.,
P.O. Box 3241
NL-2280 GE Rijswijk (NL)

(64) Method for immobilizing ecologically harmful, organic or inorganic compounds.

(67) The invention relates to a method for immobilizing ecologically harmful, organic or inorganic compounds, by mixing these compounds in the presence of water with a fixant which comprises an absorbent and allowing the mixture to set, after the addition of an inorganic hydraulic binder, to obtain a hard, stone-like material, wherein the absorbent used in the fixant is optionally pre-treated activated carbon, cellulose or a cellulose derivative. The activated carbon used preferably has been sulphurized or treated with a silicon-containing organic reagent. The fixant further contains, according to an expedient embodiment, at least one coordination complex-forming agent which, in particular, is selected from an iron, manganese or aluminium salt or comprises a combination thereof.

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The invention relates to a method for immobilizing ecologically harmful, organic or inorganic compounds, by mixing these compounds in the presence of water with a fixant which comprises an absorbent and allowing the mixture to set, after the addition of an inorganic hydraulic binder, to obtain a hard, stone-like material.

- 5 Such a method is known from the European Patent No. 0 398 410 and comprises the use of a modified clay as an absorbent for absorbing organic molecules.

As described in this publication, the layer spacing of the clay layers first has to be increased, in order to obtain good absorption efficiency with respect to the absorption of organic molecules, whereas after absorption, in order to counteract leaching of the absorbed material, the layer spacing of the clay layers has to be reduced again.

- 10 If, further, a modified clay is to be used for immobilizing a mixture of various organic and inorganic chemical compounds it is usually necessary for either a non-modified clay to be present at the same time or for the modified clay still to have non-modified sites suitable for absorption. This ensures that both hydrophobic and hydrophilic sites are available for binding various ecologically harmful compounds. In such cases it is therefore necessary to know in advance, reasonably accurately, the composition of the material to be immobilized. In practice this will, however, not always be the case.

An absorbent has now been found which is suitable for use in a method of the abovementioned type, which completely overcomes the drawbacks associated with the use of clay.

- 15 To this end, the invention is characterized in that the absorbent used in the fixant is optionally pretreated activated carbon, cellulose or a cellulose derivative.

The use of such absorbents has surprisingly led to much more efficient immobilization, in particular if high concentrations of organic pollutants are present.

- The absorbent used is preferably sulphurized activated carbon; according to an expedient embodiment an activated carbon sulphurized to approximately 5 % of sulphide. Such a material is found to be particularly suitable for binding various cations such as salts of cadmium, lead, copper, mercury and zinc.

- On the other hand, particularly advantageous binding and immobilization of strongly anionic substances such as fluorides and chlorides is obtained, if activated carbon is used which has undergone a pretreatment with a silicon-containing organic reagent. The effect of such a treatment is that said organic reagent is absorbed in the activated carbon, whereupon the anionic substance can then be bound by the absorbed reagent. The silicon-containing reagent can therefore be regarded as an active "contaminant" for the carbon.

- For that matter, the activated carbon or cellulose has been found to be particularly suitable for binding mineral oil. The compressive strength of a sandy soil contaminated with mineral oil was found, after mixing with a cement and setting for 30 days, even to be much more favourable than that of a similar sample where instead of activated carbon bentonite had been used. It should be noted in this context that the compressive strength of a set, stone-like material is related to the leaching values, in the sense that for a higher compressive strength a lower leaching value is obtained in leaching tests.

For the purpose of an expedient version of the method according to the invention, the absorbent used is methyl cellulose.

- 40 Preferably, the fixant further comprises at least one coordination complex-forming agent which preferably serves for the formation of a coordination complex with organic and in particular aromatic compounds. Aromatic compounds present in the material to be immobilized then, on the one hand, can be fixed as a coordination complex and, on the other hand, be coupled as such or via said complex to or in the pores of the activated carbon or the cellulose derivative.

- 45 The coordination complex-forming agents used are preferably a metal salt, in particular an iron, manganese or aluminium salt or a combination thereof. Such ions are found to be able, owing to their 3d electrons, to form a strong bond to the π electron cloud of aromatic compounds such as polycyclic aromatic hydrocarbons, PCBs and the like which are usually present as a microcontaminant, or a material contaminated with acid sludge, where up to tens of per cent of organic pollutants can be present.

- 50 The iron salt used is preferably a ferrous or ferric salt, such as the sulphate, nitrate, halide or hydroxide.

The manganese salt expediently is a sulphate, nitrate, oxide or halide; while the aluminium salt preferably is the sulphate, nitrate, oxide or halide.

It is further found that at least partial replacement of the iron salt used as the complexing agent by a corresponding cobalt salt results in beneficial effects.

- 55 The aim of the method according to the invention is to immobilize ecologically harmful organic and inorganic compounds by fixing these compounds by means of a fixant and incorporating the product obtained in a cement matrix. It was found that leaching of a number of compounds can be considerably reduced by also incorporating an oxidant in the fixant. Persulphate and permanganate were found to give

good results to this end.

It was further found to be advantageous for the method according to the invention for the fixant additionally to contain a calcium source, preferably consisting of gypsum or optionally slaked lime. The gypsum used can be the anhydrite, the hemihydrate or the dihydrate thereof.

The inorganic hydraulic binder to be used in the present method is preferably selected from a cement, ground and optionally granulated blast furnace slags, ground and/or porous granulated steel slags, powder-coal fly ash, thermally treated paper residue or a mixture thereof.

The invention further relates to a fixant suitable for use in the immobilization of ecologically harmful organic or inorganic compounds, said fixant being characterized in that it consists of up to 25 % by weight of an iron and/or cobalt salt, up to 25 % by weight of a manganese salt, from 15 to 60 % by weight of optionally sulphurized activated carbon, or a cellulose derivative, together with up to 25 % by weight of an oxidant.

Expediently, the fixant further contains up to 15 % by weight of an aluminium salt and, if desired, up to 40 % of a calcium source.

The invention will be described below in more detail with reference to the following examples.

EXAMPLE 1

Treatment of sludge containing mercury compounds and organic compounds.

The material to be investigated related to a sludge-like residue which contained approximately 20 % of oil-like compounds (mineral oil, volatile aromatic compounds), 35 % of water and 1 % of metallic mercury. The material was mixed with 35 % (per cent by weight) of a mixture whose composition is reproduced below:

Portland cement	55 %
Ground granulated blast furnace slag	30 %
Gypsum	3.5 %
Iron (III) chloride	2 %
Manganese sulphate	2 %
Activated carbon	7 %
Trimercaptotriazine trisodium salt	0.5 %

After mixing, the material was allowed to set at room temperature for a period of 30 days. The result was a shaped product having a strength of 2.8 MPa which, when subjected to a leaching test (on crushed material) showed leaching of mercury of a few ppb and of oil-like components of only a few ppm.

Upon replacement of 10 % of the Portland cement by powder-coal fly ash, comparable results were obtained. Replacement of 5 % of the Portland cement by ground steel slags or thermally treated paper residue gave comparable results. Replacement of the activated carbon by cellulose resulted in an outwardly similar product, from which leaching of oil-like components was admittedly somewhat higher (factor 2), but still quite acceptable.

Replacement of the activated carbon by modified bentonite (organophilic clay) resulted in a product which in a physical respect was clearly inferior to products in which activated carbon or cellulose had been used; in fact, no compression strength at all had developed. Leaching of mercury was, probably owing to a lack in strength, higher than in the previously described specimens (factor 12), leaching of oil-like components was higher by a factor of 33 than when activated carbon was used.

Replacement of the activated carbon by activated carbon being sulphurized with about 5% of sulphide resulted in product, from which mercury and oil-like components could no longer be detected in a leaching test.

The same applies for the use of activated carbon being treated with a silicon-containing organic reagent.

EXAMPLE 2Soil purification residue

The material to be examined in this case related to a residue of extractive soil purification, which in addition to approximately 8 per cent of mineral oil contained a few hundred ppm of PAH, chlorinated solvents (tri, per), cadmium, mercury and arsenic, 1,300 ppm of zinc and 4,000 ppm of lead. The material further contained approximately 40 % of water.

The material was mixed with 30 % of a mixture whose composition is reproduced below:

Portland cement	53 %
Ground granulated blast furnace slag	30 %
Gypsum	3.5 %
Iron (III) chloride	2 %
Manganese sulphate	2 %
Aluminium sulphate	1 %
Potassium persulphate	2 %
Activated carbon	5 %
Slaked lime	1 %
Trimercaptotriazine trisodium salt	0.5 %

After mixing the material was allowed to set at room temperature for 30 days. The result was a shaped material (compressive strength: 4.6 MPa), which, when a leaching test was carried out on crushed material, showed leaching of mineral oil, PAH, chlorinated solvents and zinc at the ppm level and of arsenic, cadmium, mercury and lead at the ppb level.

It was felt that the leaching of, in particular, PAH and chlorinated solvents was non-optimal. The experiment was therefore repeated, use being made, instead of activated carbon, of methyl cellulose; the results were comparable, except for the observed leaching for PAH, which was higher by a factor of 6. Employing modified bentonite instead of activated carbon did result in lower leaching for the chlorinated solvents and PAH (factor 82 and 5, respectively), but, probably owing to the poorer physical qualities of the specimens (compressive strength 0.8 MPa), considerably more mineral oil (factor 130) and arsenic (factor 11) was leached in the leaching test.

The experiment was then repeated, 2 % of the activated carbon being replaced by the modified bentonite. After setting, a physically acceptable product was obtained (compressive strength: 3.6 MPa). Leaching of chlorinated solvents decreased by a factor of 74, and leaching of PAH decreased by a factor of 4. Leaching of the other compounds studied remained comparable.

EXAMPLE 3Sandy soil mixed with diesel oil

In order to gain an insight into compression strength developed after setting when activated carbon, cellulose and organophilic clay were used, a sandy soil which had been manually admixed with 10 % of diesel oil, was mixed with 20 % of water and 25 % of a mixture of the following composition:

Portland cement	55 %
Ground granulated blast furnace slag	35 %
Manganese sulphate	2.5 %
Iron (III) chloride	2.5 %
"X"	5 %

Experiment A: "X" = activated carbon

Experiment B: "X" = cellulose

Experiment C: "X" = modified bentonite

After allowing to set at room temperature for 30 days, compressive strengths were determined. A gave a compressive strength of 4.2 MPa, B gave a compressive strength of 3.8 MPa, and C gave a compressive

strength of 1.5 MPa.

EXAMPLE 4

- 5 Treatment of blasting-grit residue having the composition given in Table 1:

Table 1

Parameter	Measured amount (mg/kg d.m.)
SO ₄	3.700
CN (free)	53
CN (total)	64
As	20
Cd	4,2
Co	34
Cr	100
Cu	2.900
Hg	24
Mo	32
Ni	160
Pb	1.700
Sn	300
Zn	5.900
PAH (total)	100
Mineral oil (GC)	450
Volatile aromatics	34
Volatile chlorinated compounds	n.d.
Cl (as extractable organic halogen)	350
n.d. means non-detectable	

This residue has been treated with fixant A comprising activated carbon and with fixant B comprising organophilic clay, said fixants having the following compositions (% w/w with respect to the blasting grit residue):

Additive	A	B
Portland cement	12,42	12,42
Blast furnace cement	11,07	11,07
Gypsum	0,81	0,81
MnSO ₄	0,675	0,675
FeCl ₃	0,405	0,405
K ₂ S ₂ O ₈	0,54	0,54
Trimercaptotriazine trisodium salt	0,5	0,5
Organophilic clay	-	1,08
Activated carbon	1,08	-
Total	27,5	27,5

After mixing, the materials were allowed to set for a period of 28 days at room temperature, to obtain immobilisates A and B.

Thereafter the composition of the cured immobilisates has been determined, see table 2.

Table 2

Parameter	Measured amount; immobilisate A (mg/kg d.m.)	Measured amount; immobilisate B (mg/kg d.m.)
SO ₄	19.500	20.000
CN (free)	7,9	12
CN (total)	13	13
As	15	15
Cd	6,0	3,8
Co	22	23
Cr	130	110
Cu	1.700	1.800
Hg	14	12
Mo	16	17
Ni	110	110
Pb	750	750
Sn	140	190
Zn	3.500	3.200
PAH (total)	55	95
Mineral oil (GC)	700	890
Volatile aromatics	1,2	1,2
Volatile chlorinated compounds	n.d.	n.d.
Cl (as extractable organic halogen)	240	290

The data given in table 2 show a remarkable reduction in the amount of cyanide and of volatile aromatics. These data have been determined in the compositions A and B by means of an extraction test for aromatics and by means of nitrohydrochloric acid for inorganic components to show the immobilisation efficiency of the process of the invention. The treatment with additive A results in a better immobilisation effect with respect to PAH's than additive B.

The leachability of the obtained products have also been investigated by means of the diffusion test. More specifically, the cumulative emissions over a period of 64 days of the relevant heavy metals and anions from the immobilisates A and B have been measured. The results thereof are given in table 3:

Table 3

Parameter	Unit	Immobilisate A	Immobilisate B
SO ₄	mg/m ²	4.989	6.840
As	mg/m ²	n.d.	n.d.
Cd	mg/m ²	n.d.	n.d.
Co	mg/m ²	n.d.	n.d.
Cr	mg/m ²	1,53	1,58
Cu	mg/m ²	46,33	61,20
Hg	mg/m ²	n.d.	n.d.
Mo	mg/m ²	15,68	18,36
Ni	mg/m ²	n.d.	n.d.
Pb	mg/m ²	n.d.	n.d.
Sn	mg/m ²	3,56	86,40
Zn	mg/m ²	n.d.	n.d.
n.d. means non-detectable.			

The compressive strengths of the immobilisates A and B have also been measured after 3 days and after 28 days:

Compressive strength (N/mm ²)	Immobilisate A	Immobilisate B
After 3 days	0,41	0,45
After 28 days	4,35	4,21

The above-given results show clearly the superior effect of fixant A over fixant B with respect to the immobilisation of especially heavy metals.

With respect to the increased amount of sulfate found in the leachate of immobilisates A and B it is observed that gypsum ($\text{CaSO}_4 \cdot x \text{H}_2\text{O}$) has been used as a hardening regulator in both additives, resulting in an increased amount thereof in the leachates.

Claims

- Method for immobilizing ecologically harmful, organic or inorganic compounds, by mixing these compounds in the presence of water with a fixant which comprises an absorbent and allowing the mixture to set, after the addition of an inorganic hydraulic binder, to obtain a hard, stone-like material, **characterized in that** the absorbent used in the fixant is optionally pretreated activated carbon, cellulose or a cellulose derivative.
- Method according to claim 1, **characterized in that** the absorbent used is sulphurized activated carbon.
- Method according to claim 1 or 2, **characterized in that** the absorbent used is activated carbon sulphurized with up to 5 % of sulphide.
- Method according to claim 1, **characterized in that** activated carbon is used which has been treated with a silicon-containing organic reagent.
- Method according to claim 1, **characterized in that** the absorbent used is methyl cellulose.
- Method according to one or more of the claims 1 to 5, **characterized in that** the fixant further comprises at least one coordination complex-forming agent.
- Method according to claim 6, **characterized in that** the coordination complex-forming agent used is a metal salt, in particular an iron, manganese or aluminium salt or a combination thereof.
- Method according to claim 7, **characterized in that** the iron salt used is ferrous or ferric sulphate, nitrate, halide or hydroxide.
- Method according to claim 7, **characterized in that** the manganese salt used is a sulphate, nitrate, oxide or halide.
- Method according to claim 7, **characterized in that** the aluminium salt used is a sulphate, nitrate, oxide or halide.
- Method according to claims 7 or 8, **characterized in that** the iron salt is replaced at least in part by a cobalt salt.
- Method according to one or more of the claims 1 to 11, **characterized in that** the fixant further contains an oxidant, in particular a persulphate or a permanganate.
- Method according to one or more of the claims 1 to 12, **characterized in that** the fixant further contains a calcium source, preferably gypsum or optionally slaked lime.

14. Method according to one or more of the claims 1 to 13, **characterized in that** the inorganic hydraulic binder used is a binder selected from a cement, ground and optionally granulated blast furnace slags, ground and/or porous granulated steel slags, powder-coal fly ash, thermally treated paper residue or a mixture thereof.

15. Fixant suitable for use in the method according to one or more of the claims 1 to 14, **characterized in that** the fixant consists of up to 25 % by weight of an iron and/or cobalt salt, up to 25 % by weight of a manganese salt, from 15 to 60 % by weight of optionally sulphurized activated carbon, or a cellulose derivative, together with up to 25 % by weight of an oxidant.

16. Fixant according to claim 15, **characterized in that** the fixant further contains up to 15 % by weight of an aluminium salt and, if desired, up to 40 % of a calcium source.



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EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0451

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP,A,0 535 757 (PELT & HOYKAAS) 7 April 1993 * page 3, line 40-46 * * page 4, line 36-42 * * page 8, line 49-55 * ----	1-16	A62D3/00
X	WO,A,92 16317 (LANDFILL SERVICE CORPORATION) 1 October 1992 * page 3, column 22 - page 4, column 10 * * page 9, column 9-34 * * claims * ----	1,5	
X	FR,A,2 302 970 (QMATERIEL PERRIER) 1 October 1976 * claims * ----	1,5	
X	EP,A,0 149 501 (PELT & HOYKAAS) 24 July 1985 * claim 9 * ----	1-4	
A	EP,A,0 535 758 (PELT & HOYKAAS) 7 April 1993 ----		TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	DATABASE WPI Week 7942 Derwent Publications Ltd., London, GB; AN 79-76659B & SU,A,643 573 (BALTAIS G E) * abstract * -----	1,5	A62D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		1 June 1995	Dalkafouki, A
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : number of the same patent family, corresponding document	